New Silica Removal Technique by Vacuum Heating toward High-Performance Cryosorption Pumps Based on Biomass-Based Activated Carbon

Yuto YANAGIHARA[1)], Takanori MURASE[1)], Hiroyuki NOTO[1)], Kunihiro OGAWA[1,2)], Akihiro SHIMIZU[1,2)], Mitsutaka ISOBE[1,2)], Kazuki NAGAHARA[1)], Hiroyuki TANOUE[1)], Sho NAKAGAWA[1)], Yuki HAYASHI[1,2)], Ngat T.H. PHAM[3)], Tomohiro SHIOZAKI[3)], Toshiaki SOGABE[3)] and Mudtorlep NISOA[4)]

[1)] *National Institute for Fusion Science, National Institutes of Natural Sciences, 322-6 Oroshi-cho, Toki 509-5292, Japan*

[2)] *The Graduate University for Advanced Studies, SOKENDAI, 322-6 Oroshi-cho, Toki 509-5292, Japan*

[3)] *ANAORI CARBON Co., Ltd., 6-20 Hatakeda-cho, Ibaraki 567-0028, Japan*

[4)] *Functional Materials & Nanotechnology CoE, Walailak University, Nakhon Si Thammarat, 80160, Thailand*

(Received 15 December 2023 / Accepted 9 January 2024)

We developed a new silica (SiO_2) removal technique that can maximize biomass-based activated carbon adsorption performance. SiO_2 removal is one of the key processes in making activated carbon suitable for cryosorption pumps in fusion machines. In this study, we employed an evaporation process to remove SiO_2 by high-temperature vacuum heating. The charcoal made from rice straw was heated at 1800°C for 1 h at approximately 10 Pa in a vacuum furnace. We found that SiO_2 amount was significantly reduced from 15.8 wt% to 4.20 wt% due to vacuum heating. In addition, the result of surface element mapping analysis using energy-dispersive X-ray spectroscopy (EDX) indicated a considerable decrease in the oxygen content of SiO_2. We demonstrated the great potential of activated carbon derived from rice straw as an adsorbent for high-performance cryosorption pumps.

Keywords: cryosorption pump, activated carbon, silica, vacuum heating, unutilized biomass

DOI: 10.1585/pfr.19.1205012

The Large Helical Device located at the National Institute for Fusion Science is equipped with cryosorption pumps that use activated carbon from coconut shells as an adsorbent for gas particles [1]. Activated carbon is a porous material that undergoes chemical [2] or physical activation [3] after the carbonization of carbonaceous sources. Small particles, such as hydrogen, are adsorbed in micropores with diameter less than 2 nm. An increased number of mesopores, ranging from 2 nm to 50 nm in diameter, within activated carbon enhances the pumping speed because pores provide a pathway for the particles [4]. Removing silica (SiO_2) from carbonaceous materials is a known method to produce mesopore-rich activated carbon [5]. The sites occupied by SiO_2 become a mesopore. Herein, we focus on the use of rice straw, an unutilized biomass, as a raw material for preparing the activated carbon of cryopumps. Rice straw contains a considerable number of SiO_2, making it a suitable raw material for the production of activated carbon with mesoporous properties [6]. In addition, from an industrial point of view, mesoporous activated carbon is expected to be a capacitor with excellent rate capability [7].

Generally, a strong alkaline cleaning solution, such as sodium hydroxide solution, is employed for SiO_2 removal. However, due to surface tension, these solutions have limitations in effectively permeating the carbon structure. Therefore, not all SiO_2 contained within rice straw can be removed [8, 9]. To solve this, we employed an evaporation process to remove SiO_2 through high-temperature vacuum heating by thermal conduction, specifically at temperatures equal to or higher than 1710°C, which aligns with the melting point of SiO_2, ultimately reaching 1800°C. In this study, we focus on tracking changes in SiO_2 content within rice straw charcoal by high-temperature vacuum heating.

We refer to carbonized rice straw as charcoal. The procedure for producing charcoal by high-temperature vacuum heating is as follows. First, the rice straw was cut into pieces approximately 10 mm in size and packed into a stainless steel cylindrical container of $\varphi 40 \times 190$ mm. A lid with a pipe of $\varphi 6.5$ mm in the center was then welded to the container. The container was heated with a burner to 200°C, completing the carbonization of rice straw. Second, the container was placed in a tubular furnace. Note that the pipe was connected to a vacuum pump to draw out the impurity gasses generated from the charcoal. The furnace was held at 1000°C for 1 h, and the container was maintained at approximately 100 Pa. In this step, the charcoal

author's e-mail: yanagihara.yuto@nifs.ac.jp

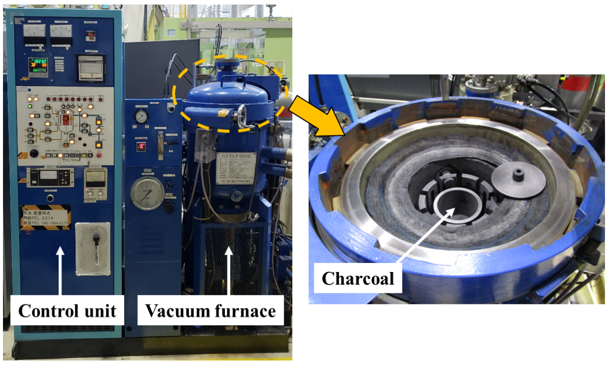


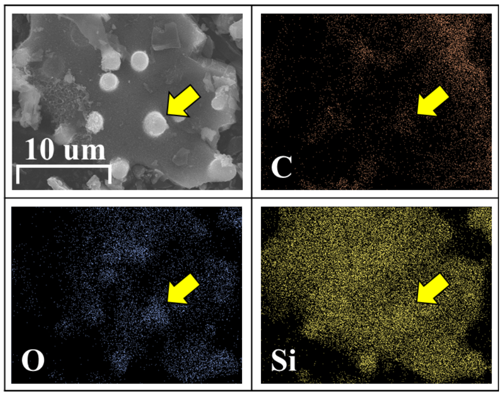
Fig. 1 Setup of high-temperature vacuum heating.

was degassed to prevent contamination of the equipment in later processes. The charcoal was then collected from the container and crushed. Finally, the charcoal was heated in a vacuum furnace, different from the furnace used in the previous step, at 1800°C for 1 h at approximately 10 Pa, as shown in Fig. 1. In this step, the SiO_2 was removed.

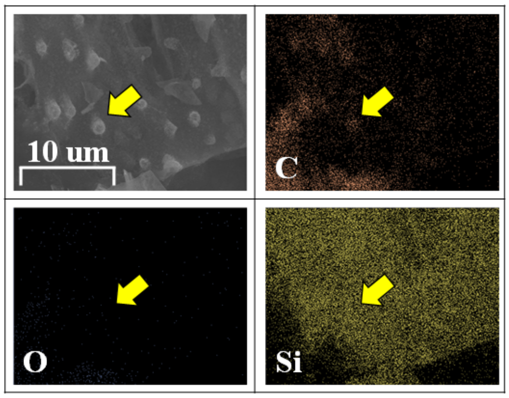
Si compound measurements were performed on charcoal before and after vacuum heating at 1800°C. The weight percentage of SiO_2 was evaluated indirectly by measuring the amount of silicon (Si) compounds in charcoal using inductively coupled plasma atomic emission spectroscopy. The amount of SiO_2 decreased from 15.8 wt% to 4.20 wt% due to vacuum heating.

The charcoal surfaces were examined using a field-emission scanning electron microscope, and their surface element analysis was performed using energy-dispersive X-ray spectroscopy (EDX). We focused on a projecting structure that contains a considerable amount of SiO_2 in rice straw. Figure 2 shows the results of elemental mapping by EDX. Yellow arrows indicate the projecting structures. Carbon, the base material of rice straw, was detected on both the charcoal samples. Oxygen was detected on the charcoal projecting structure before vacuum heating, as shown in Fig. 2 (a). Meanwhile, almost no oxygen was detected on the charcoal after vacuum heating, as shown in Fig. 2 (b). Furthermore, an analysis of Si distribution showed that Si was widely present on the charcoal surface before and after vacuum heating. Based on these results, it appears that the oxygen content of SiO_2 in charcoal is reduced by vacuum heating, and Si remains on the surface of charcoal. This Si could interfere with pore formation during the activation process and may need to be removed as well as SiO_2.

In summary, we demonstrated a substantial SiO_2 reduction in rice straw by applying a new method, i.e., high-temperature vacuum heating. The resulting charcoal has a great potential to serve as an activated carbon material with considerable mesoporous characteristics. In the future research, we will perform a comparison of SiO_2 removal with conventional methods using the same rice straw. Additionally, we will produce highly functional activated carbon using the proposed vacuum-heated charcoal and assess its pumping speed in a cryosorption pump.



(a) Charcoal before vacuum heating.



(b) Charcoal after vacuum heating.

Fig. 2 Mapping of surface elements on the projecting structure by EDX.

[1] T. Murase *et al.*, Plasma Fusion Res. **11**, 1205030 (2016).
[2] Z. Heidarinejad *et al.*, Environ. Chem. Lett. **18**, 393 (2020).
[3] B. Sajjadi *et al.*, Rev. Chem. Eng. **35**, 735 (2019).
[4] T. Murase *et al.*, J. Plasma Fusion Res. **93**, 213 (2017) (in Japanese).
[5] D. Liu *et al.*, Chin. Chem. Lett. **30**, 1315 (2019).
[6] B.A. Goodman, J. Bioresour. Bioprocess. **5**, 143 (2020).
[7] S. Shiraishi *et al.*, Electrochemistry **69**, 440 (2001).
[8] N. Abd-Talib *et al.*, Mater. Today-Proc. **31**, 145 (2020).
[9] N.M. Hieu *et al.*, Procedia Chem. **15**, 308 (2015).